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(54) **Gas-tight sintered translucent aluminium oxide.**

(57) The invention relates to gas-tight sintered translucent aluminium oxide having a density of at least 99.5%, which contains at most 1000 ppm by weight of MgO. According to the invention, the aluminium oxide also has a content of Er_2O_3 lying between 20 ppm by weight and 200 ppm by weight. The material thus obtained has a great mechanical strength, a high resistance to especially attack by sodium and a satisfactory translucence. Thus, the material is very suitable for use as wall material for the discharge vessels of high-pressure discharge lamps.

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"Gas-tight sintered translucent aluminium oxide"

The invention relates to gas-tight sintered translucent aluminium oxide having a density of at least 99.5% and containing MgO in a quantity of at most 1000 ppm by weight. The invention further relates to a method of manufacturing an article from this material. Such a material is known from USP 3,905,845. The known material is gas-tight, is highly translucent and is widely used _inter alia_ in discharge vessels of high-pressure discharge lamps. Besides MgO, Y_2O_3 and La_2O_3 are added in order to obtain a satisfactory density and a regular crystal size distribution of the sintered material. However, the addition of Y_2O_3 and La_2O_3 can give rise to ß aluminate crystal structures, which adversely affect the durability of the material. Especially in the case of the use as a wall of a discharge vessel in which sodium is incorporated, it is found that the ß aluminate structure can be very readily attacked by the Na.

The invention has for its object to provide a measure for obtaining gas-tight sintered translucent aluminium oxide having a regular crystal size distribution and being free from ß aluminate structure.

For this purpose, according to the invention, a material of the kind mentioned in the opening paragraph is characterized in that the aluminium oxide also contains erbium (Er) in a quantity, expressed in Er_2O_3, of at least 20 ppm by weight and at most 200 ppm by weight.

The material according to the invention has a regular crystal size distribution and is highly translucent in sintered form. Besides, the material is found to be highly durable against the attack by sodium. An advantage of the material is that especially Ca impurity in the material is segregated at crystal boundaries in an ErCa aluminate. It is further ascertained that the ErCa structure is not of the ß type, which has a favourable influence on the durability against the attack by sodium. This, the material according to the invention is particularly suitable for use as wall material of discharge vessels of

high-pressure discharge lamps.

A content of Er lower than 20 ppm by weight results in that the material has an irregular crystal size distribution; especially the surface is coarse-crystalline and has many pores. This is due to the evaporation of MgO from the surface layer during sintering, as a result of which an unhindered crystal growth can occur.

A content of Er higher than is required for obtaining a regular crystal size distribution is found to lead to an irregular grain growth. It has been found that even under very favourable conditions with an Er content higher than 200 ppm by weight the phenomenon of irregular grain growth occurs, as a result of which even a secondary crystallization can occur. Both the density and the extent of translucence are unfavourably influenced thereby.

The addition of Er_2O_3 as a dopant during sintering of aluminium oxide is known from literature. (Yogyo-Kyokai-Shi 87, No. 12, 1979, pp. 633-641; 88, No. 11, 1980, pp. 660-673; 88, No. 9, 1980, pp. 531-538). In all cases, however, quantities of 500 ppm by weight or more are concerned. Gas-tight translucent aluminium oxide is found to be not realizable at such high concentrations of Er, however.

In a preferred embodiment of a material according to the invention, the content of MgO is lower than 500 ppm by weight and the Er content, expressed in Er_2O_3 is at most 130 ppm by weight. This material has the advantage that a strong homogeneous gas-tight and translucent material is obtained having a very high durability against attack by sodium. The small quantity of MgO is found to be favourable for the durability of the material. A possible explanation for this fact is that no Mg-containing second-phase separation occurs. The Er_2O_3 promotes that in spite of the small quantity of MgO a homogeneous crystal size distribution is nevertheless obtained in the material.

An article of gas-tight sintered translucent aluminium oxide according to the invention is preferably manufactured by means of a method which is characterized in that an MgO compound is added to a powder mixture of Al_2O_3 in that the Al_2O_3 powder thus obtained is shaped preferably after disagglomeration into a desired moulding and is then heated in an oxidizing atmosphere at a temperature between 1150^o and 1400^o, in that subsequently a desired quantity of Er_2O_3 is added to the moulding by impregnation in an Er-containing

solution, and in that thereafter the moulding is sintered in hydrogen or in a vacuum at a pressure of at most 0.13 Pa at a temperature of at most 1800°C.

Preferably, the Er-containg solution consists of an Er acetyl acetonate solution in alcohol. An advantage is that this solution can be obtained in a simple manner and that impregnation of mouldings in this solution leads to reasonably reproducible results. A further advantage is that in this method the content of Er_2O_3 added to the mouldings can be varied in a very simple manner on the one hand by variation in time of impregnation and on the other hand by variation in Er concentration in the solution.

Example.

A number of cylindrical tubes have been manufactured using as starting material disagglomerated Al_2O_3 powder having a purity of 99.99% and a specific surface area of 6 m/g, to which an MgO dopant is added during the preparation of a kneading mass, whereupon these tubes are shaped by means of extrusion and are then baked out in air at a temperature of 1280°C. Subsequently, a number of the cylindrical tubes thus obtained are immersed in a solution of Er acetyl acetonate in alcohol. By variation in the concentration of the Er acetyl acetonate and in the time of immersion, different Er dopant contents are obtained.

Subsequently, the tubes are sintered to translucent gas-tight tubes. The sintered tubes have a wall thickness of 6 mm. A large number of properties of the tubes thus obtained have been determined. The following table indicates the compositions and the properties of the different articles.

In the columns under the headings G_{max} and G_{gem}, the maximum crystal size and the average crystal size, respectively, each expressed in µm, are stated. This crystal size is determined by means of electron microscopy.

The mechanical strength expressed in MN/m^2, is stated in the column under the heading σ_f and is determined by means of the ring test method. The extent of translucence is determined by means of a rectilinear light transmission measurement and the results are stated in the column under the heading RLD, expressed in a relative measure. The tubes are sintered for 5 hours at a temperature of 1750°C in

hydrogen.

A penetration depth of sodium of a number of tubes is determined by arranging the tubes concerned in a molybdenum vessel, which also contains amalgam comprising 30% by weight of sodium and is heated for 100 hours at 1100^{o}O. Subsequently, the tubes are given polished and etched cross-sections, at which the penetration depth of sodium into the crystals is determined by means of microspectral analysis.

The tubes enumerated 2 to 6 consist of aluminium oxide according to the invention. In comparison with a tube without Er (No. 1) or having too high an Er content (7), the tubes 2 to 6 have a regular crystal size distribution. The average crystal size of the tubes 2 to 6 is comparatively small as compared with that of the tubes 1 and 7, which accounts for the lower values for the translucence of the tubes 2 to 6 with respect to that of the tubes 1 and 7. On the contrary, the mechanical strength is considerably greater.

The sodium penetration depth of the tubes 1, 3 and 4 is determined by means of the method described above. It then appears that for the tube 1 the penetration depth is larger than 250 µm and that an attack on the crystal boundaries can be observed throughout the wall thickness. For the tubes 3 and 4, the penetration depth is 600 and 50 µm, respectively, while in none of the two cases a preferential attack of the crystal boundaries can be observed.

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TABLE

No.	MgO % by weight	Er_2O_3 % by weight	G_{max} µm	G_{gem} µm	σ_f	RLD	penetration depth Na
1	300	0	> 300	20	135	157	> 250 µm crystal size overall wall thickness
2	300	20	35	12	296	138	
3	300	50	35	12	296	122	60 µm with preferential crystal boundary
4	300	125	100	18	238	142	50 µm with preferential crystal boundary
5	1000	20	35	12	322	131	
6	1000	50	60	14	251	125	
7	1000	390	150	30	187	167	

1. A gas-tight sintered translucent aluminium oxide having a density of at least 99.5% containing MgO in a quantity of at most 1000 ppm by weight, characterized in that the aluminium oxide also contains erbium (Er) in a quantity, expressed in Er_2O_3, of at least 20 ppm by weight and at most 200 ppm by weight.

2. Aluminium oxide as claimed in Claim 1, characterized in that the MgO content is smaller than 500 ppm by weight and the Er content, expressed in Er_2O_3, is at most 130 ppm by weight.

3. A method of manufacturing an article from gas-tight sintered aluminium oxide as claimed in Claim 1 or 2, characterized in that an MgO compound is added to a powder mixture of Al_2O_3, in that the Al_2O_3 powder thus obtained is shaped, preferably after disagglomeration, into a desired moulding and is then heated in an oxidizing atmosphere at a temperature between 1150^{o}C and 1400^{o}C, in that a desired quantity of Er_2O_3 is then added to the moulding by impregnation in an Er-containing solution, and in that thereafter the moulding is sintered in hydrogen or in a vacuum at a pressure of at most 0.13 Pa at a temperature of at most 1800^{o}C.

4. A method as claimed in Claim 3, characterized in that the Er-containing soluiton consists of an Er acetyl acetonate solution in alcohol.

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EUROPEAN SEARCH REPORT

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EP 86 20 1527

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	CHEMICAL ABSTRACTS, vol. 94, no. 12, March 1981, page 323, abstract no. 89034a, Columbus, Ohio, US; S. OHTA et al.: "Effects of erbium(III) oxide addition on sintering of alumina", & YOGYO KYOKAISHI 1980, 88(9), 531-8	1-3	C 04 B 35/10 H 01 J 61/30
A	CHEMICAL ABSTRACTS, vol. 81, no. 26, December 1974, page 363, abstract no. 175149e, Columbus, Ohio, US; & JP-A-74 15 447 (NIHON TOKUSHU TOGYO CO. LTD.) 15-04-1974	1-3	
A	US-A-3 834 915 (J.J. CLEVELAND) * Claims 1-3 *	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 040 499 (NGK INSULATORS) * Claims 1-5; page 4, lines 16-31 *	1-3	C 04 B H 01 J
A	FR-A-2 179 807 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) * Claims 1-7; page 4, lines 28-37 *	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-12-1986	SCHURMANS H.D.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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